Accepted Manuscript

Title: Adsorptive interaction between 1,5-pentanediol and MgO-modified ZrO₂ catalyst in the vapor-phase dehydration to produce 4-penten-1-ol





Please cite this article as: Hailing Duan, Masaki Unno, Yasuhiro Yamada, Satoshi Sato, Adsorptive interaction between 1,5-pentanediol and MgO-modified ZrO2 catalyst in the vapor-phase dehydration to produce 4-penten-1-ol, Applied Catalysis A, Generalhttp://dx.doi.org/10.1016/j.apcata.2017.07.048

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



A revised manuscript for the original paper submitted to the journal of *Appl. Catal. A: Gen.* Re: APCATA-D-17-00953

Adsorptive interaction between 1,5-pentanediol and MgO-modified ZrO₂ catalyst in the vapor-phase dehydration to produce 4-penten-1-ol Hailing Duan, Masaki Unno, Yasuhiro Yamada, Satoshi Sato*

Graduate School of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan

* Corresponding author. Tel. +81-43-290-3376; fax: +81-43-290-3401

E-mail address: satoshi@faculty.chiba-u.jp (S. Sato)

Adsorptive interaction between 1,5-pentanediol and MgO-modified ZrO₂ catalyst in the vapor-phase dehydration to produce 4-penten-1-ol Hailing Duan, Masaki Unno, Yasuhiro Yamada, Satoshi Sato*

Graduate School of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan



Graphical abstract

Highlights

- Dehydration of 1,5-pentanediol was investigated over modified monoclinic ZrO₂ at 400 °C.
- Stable catalytic activity of MgO/ZrO₂ was observed at conversion of 96% with the 4-penten-1-ol selectivity >76%.
- Adsorptive interaction between 1,5-pentanediol and MgO/ZrO₂ was stronger than other combinations.
- A strong adsorptive interaction between 1,4-butanediol and CaO/ZrO₂ was also observed.

Abstract

Vapor-phase catalytic dehydration of 1,5-pentanediol (1,5-PDO) was investigated over monoclinic ZrO₂ catalysts modified with basic oxides. An unsaturated alcohol, 4-penten-1-ol (4P1OL), was produced together with the formation of tetrahydropyran, δ-valerolactone, 1,4-pentadiene, pentanal, 1-pentanol, and 5-hydroxypentanal, etc. Among the modified ZrO₂ catalysts, only ZrO₂ modified with MgO enhanced the selectivity to 4P1OL efficiently. The most active modified catalyst was found to be with 20 mol% MgO and a calcination at 800 °C (MgO/ZrO₂), over which the selectivity of 4P1OL exceeded 83% at 400 °C. A pulse adsorption measurement of several chemicals clarified adsorptive interaction between a reactant and a catalyst at 220 °C: the interaction between 1,5-PDO and MgO/ZrO₂ was stronger than the other adsorbates and catalysts. Another strong adsorptive interaction between 1,4-butanediol and CaO/ZrO₂, which was effective in the dehydration of 1,4-butanediol to produce 3-buten-1-ol, was also observed.

Keywords: 1,5-pentanediol; dehydration; 4-penten-1-ol; MgO supported; modified monoclinic ZrO₂;

1. Introduction

4-Penten-1-ol (4P1OL) is one of the important industrial intermediates for polymers [1,2], aroma compounds [3,4], and medical drugs [5,6,7]. However, only a few reports were found on the preparation of 4P1OL. These reports were focused on the formation of 4P1OL from tetrahydrofurfuryl alcohol [8] and tetrahydrofurfuryl halide [9]. High yield of 4P1OL (90%) was obtained in the synthesis while the reactions must be conducted in a liquid phase with the usage of solvents. Besides, there is another possibility for 4P1OL preparation via the reaction of allyl magnesium chloride with ethylene oxide and then followed by hydrolysis [10].

In our previous reports, we have investigated the preparation of 4P1OL from 1,5pentanediol (1,5-PDO) [11-15]. 1,5-PDO is one of the most valuable chemical compounds and it is usually used in the production of polyurethanes [16], polyesters [17], and polycarbonatediols [18], etc. 1,5-PDO can be also produced from lignocellulosic biomass via the intermediates, furfural, over Pt/Co₂AlO₄ with 99% selectivity [19], and tetrahydrofurfuryl alcohol, over Rh-ReOx/SiO₂ [20], Rh-ReOx/C [21], and Ni-Y₂O₃ [22] with high conversion and ca. 90% selectivity. Thus, to realize the low-carbon society, the wide application of biomass-derived 1,5-PDO to more valuable compounds such as 4P1OL would bring great prospects.

We have investigated the dehydration of 1,5-PDO over various solid catalysts and found that monoclinic ZrO_2 (m- ZrO_2) showed high catalytic activities with 4P1OL selectivity at most 50% [11]. The catalytic activities of Yb₂O₃ were enhanced greatly with increasing calcination temperatures, especially the 4P1OL selectivity of 76.7% was obtained at the 1,5-PDO conversion of 65.9% over 800 °C-calcined Yb₂O₃ at 400 °C [11]. In₂O₃ was also found to have a high 4P1OL selectivity of 70.8% and 1,5-PDO conversion of 36.9% at 350 °C [12]. The formation rate of 4P1OL from 1,5-PDO shifted with the radii of rare earth cations

of the rare-earth oxide catalysts, which were calcined at 800 °C. The highest 4P1OL formation rate had been obtained over Lu₂O₃ (4P1OL selectivity, 77.8% at 400 °C) with the radius (0.0861 nm) smaller than Yb₂O₃ (0.0868 nm) but larger than Sc₂O₃ (0.0745 nm) [13]. Sc_{0.5}Yb_{1.5}O₃, both the average radius (0.0837 nm) and the lattice parameter (1.0318 nm) which is close to Lu₂O₃ (1.0391nm), was also reported as the most active catalyst with the 4P1OL formation rate of 1.106 mmol h⁻¹ m⁻², which is higher than that of Lu₂O₃ (0.884 mmol h⁻¹ m⁻²) [14].

In contrast to the precious rare earth catalysts, modification of an inexpensive m-ZrO₂ with 1.5 mol% of Li⁺ also efficiently increased the 4P1OL selectivity up to 75.9% whereas decreased the conversion of 1,5-PDO greatly from 50.2% to 29.7% at 400 °C [11]. With increasing the loaded Li⁺ content, it was observed that the special surface area decreased, and that the density of acidic sites decreased while the density of basic sites increased. These changes in the acid-base property suppressed the formation of the major by-products such as tetrahydropyran (THP) successfully [11]. In addition, CaO-modified m-ZrO₂ catalysts have been reported to be effective in the dehydration of 2,3-butanediol [23, 24] and 1,4-butanediol [25, 26].

In the present work, we investigated the 4P1OL formation from 1,5-PDO over m-ZrO₂ catalysts modified with basic oxides. It was found that modification of m-ZrO₂ with MgO was efficient for the enhancement of the 4P1OL selectivity. The catalytic activity of MgO/ZrO₂ was studied in detail, and the adsorption interaction between 1,5-PDO and 20-MgO/ZrO₂-800 was also evaluated to clarify the reaction mechanisms.

2. Experimental

2.1 Catalyst preparation

m-ZrO₂ (RSC-100) was supplied by Daiichi Kigenso Kagaku Kogyo Co. Ltd. LiNO₃, NaNO₃, KNO₃, Mg(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Sr(NO₃)₂, and Ba(NO₃)₂ were purchased from Wako Pure Chemical Industries, Ltd. 1,5-PDO, 4P1OL, 1,4-butanediol, 3buten-1-ol, acetone, and 1-decanol were purchased from Wako Pure Chemical Industries, Ltd.

In this study, the modification of m-ZrO₂ was conducted by incipient wetness impregnation. Each aqueous nitrate solution with the prescribed amount of metal was impregnated on m-ZrO₂ support. The impregnated samples were dried at 110 °C for 12 h and then calcined in air at a prescribed temperature for 3 h. Hereafter, the ZrO₂-supported catalysts are expressed as X-MO/ZrO₂-T, where MO means the metal oxide impregnated on the support ZrO₂, X is MO content defined as the following equation: M/(M+Zr) in molar percentage, and T represents the calcination temperature.

2.2 Catalytic reaction

The reaction was carried out in a fixed-bed flow reactor at an atmospheric pressure of carrier gas, either N₂ or H₂, with a flow rate of 30-90 cm³ min⁻¹ at 250-450 °C. After a catalyst (0.5-3.0 g) had heated at a prescribed reaction temperature for 1 h, the reactant 1,5-PDO was fed into the reactor at a feed rate of 1.65 g h⁻¹ i.e. 15.9 mmol h⁻¹. The contact time, W/F, where W is catalyst weight and F is the feed rate of 1,5-PDO, was typically 0.3 h at W = 0.5 g. The liquid effluent collected hourly was analyzed by gas chromatography (FID-GC-8A, Shimadzu, Japan) with a 30-m capillary column (InertCap WAX). The products were identified by a mass spectrometer combined with gas chromatography (GCMS-QP5050A, Shimadzu, Japan) using a 30-m capillary column (DB-WAX). The catalytic activity was evaluated by averaging the conversion and selectivity data in the initial 5 h. Both the conversion of 1,5-PDO and the selectivity to each product were defined as molar percentage.

2.3 Characterization

X-ray diffraction (XRD) patterns were recorded on New D8 ADVANCE (Bruker) using Cu K α radiation (λ = 0.154 nm) to detect the crystal structure of each catalyst. The specific surface area of catalyst was calculated by the BET method using the N₂ isotherm at -196 °C. Temperature-programmed desorption (TPD) profiles of CO₂ and NH₃ were measured to estimate the basicity and acidity of the catalysts. The numbers of basic sites were estimated from neutralization-titration curves of diluted NaOH solution, and the acidic sites were estimated with the same method by H₂SO₄ solution. The density of basic sites was calculated based on the numbers of basic sites per gram and the specific surface area of the catalyst per gram, and the detail was described as the previous report [11].

To evaluate the interaction between an adsorbate and a catalyst, adsorption experiment was carried out using a self-made pulse adsorption apparatus, which was constructed by connecting a flow line with an adsorption tube made of glass with an inside diameter of 4 mm and a thermal conductivity detector (TCD). Figure S1 in the supplementary information illustrates the outline of pulse adsorption apparatus. A catalyst sample placed in the tube had been preheated at 220 °C in He flow with a flow rate of 15 cm³ min⁻¹ at an ambient pressure. An adsorbate was introduced to the catalyst bed through injection rubber septum using a micro-syringe with the amount of 0.1 mm³ for each, and such an operation was repeated for several times. The adsorbate vaporized in He flow was carried to the catalyst bed and adsorbed on the catalyst. After adsorption-desorption cycle over the catalyst bed, the adsorbate desorbed from the catalyst bed was carried to the TCD detector, from which the TCD signal was recorded for analysis. The averaged retention time and full width at half maximum (FWHM) of the detected desorption peak were used for evaluating the adsorptive interaction.

3. Results and the catalyst characterizations

3.1. Dehydration of 1,5-PDO over modified m-ZrO₂ catalysts

The dehydration of 1,5-PDO has been investigated over several catalysts in our previous report [11]. It has been found that the main products are 4P1OL, THP, and δ -valerolactone (DVL), together with 1,4-pentadiene, pentanal, 1-pentanol, cyclopentanone, 3-penten-1-ol, 2-methyltetrahydrofuran, 3,4-dihydropyran, and 5-hydroxypentanal. In the present study, Table 1 lists the catalytic results of tetragonal ZrO₂ (t-ZrO₂), m-ZrO₂ and the modified m-ZrO₂ catalysts. m-ZrO₂ showed both higher conversion of 1,5-PDO and selectivity of 4P1OL than those of t-ZrO₂ which showed high selectivity to THP, the main by-product over m-ZrO₂. The modification of m-ZrO₂ with Li₂O, Na₂O, K₂O, CaO, SrO and BaO suppressed the 1,5-PDO conversion. In contrast, only MgO enhanced the 4P1OL selectivity of m-ZrO₂ from 62.4 to 77.7% and maintained the conversion of 1,5-PDO at ca. 60%.

Table 2 shows the catalytic activities of the modified m-ZrO₂ at different MgO contents. Increase in the MgO content from 5 to 20 mol% resulted in the slight decrease in the specific surface area while no conversion decrease was observed. Among the tested catalysts, 20-MgO/ZrO₂ showed the highest 4P1OL selectivity of 83.3 mol%. However, the excess loading of MgO with 30 mol% greatly decreased both the specific surface area and the 1,5-PDO conversion.

Table 3 summarizes the effect of calcination temperature of 20-MgO/ZrO₂ on the catalytic activities. At calcination temperatures increased from 600 to 800 °C, the conversion of 1,5-PDO almost unchanged over 20-MgO/ZrO₂ catalysts despite the decrease in their specific surface areas. On the other hand, the 4P1OL selectivity increased greatly and the THP selectivity decreased up to a calcination temperature of 800 °C. Over the 20-MgO/ZrO₂-800, the 4P1OL selectivity was 83.3% at the 1,5-PDO conversion of 59.1%. The 4P1OL formation rate was 0.67 mmol h⁻¹ m⁻²: it is smaller than the highest value (1.11

mmol h⁻¹ m⁻² at 400 °C) previously reported for $Sc_{0.5}Yb_{1.5}O_3$ with the specific surface area of 26.2 m² g⁻¹ [14]. Table S1 in the supplementary information shows the effect of calcination temperature of pure m-ZrO₂ on the catalytic activities. Over the pure m-ZrO₂ calcined at 1000 °C, the 4P1OL selectivity was 68.6% at the 1,5-PDO conversion of 50.9%. High calcination temperatures decreased the specific surface area. Therefore, the 1,5-PDO conversion decreased with increasing calcination temperature, while the 4P1OL selectivity slightly increased from 56.2 to 68.6% at the calcination temperatures from 600 to 1000 °C. The formation rate of 4P1OL simply increased: the highest 4P1OL formation rate over m-ZrO₂-1000 was 1.35 mmol h⁻¹ m⁻², whereas the selectivity was only 68.8% (Table S1). Thus, it was found that 20-MgO/ZrO₂ showed the selective catalytic features at a calcination temperature of 800 °C.

Figure 1 displays the effects of reaction temperature on the catalytic activity of 20-MgO/ZrO₂-800. The 1,5-PDO conversion increased with increasing the reaction temperature while the 4P1OL selectivity reached the highest at 400 °C. Besides, the selectivities to both THP and DVL decreased rapidly until 375 °C and then calmed down after that. Instead, the by-products such as pentanal, 1-pentanol, and 5-hydroxypentanal were produced preferentially at high temperatures over 400 °C. Thus, the most efficient reaction temperature for the 4P1OL production is 400 °C. Figure 2 also shows the stabilities of 20-MgO/ZrO₂-800 catalyst in the conversion of 1,5-PDO at 400 °C. Stable catalytic activity was observed at conversion of 96% with the 4P1OL selectivity over 75% at W/F = 1.8 h and 400 °C for 10 h of time on stream. The effect of contact time (W/F) on the catalytic dehydration is summarized in Table S2.

3.2 Characterizations of modified m-ZrO₂ catalysts

Figure 3 shows the XRD patterns of MgO/ZrO₂ catalysts. The major diffraction peaks attributed to monoclinic phase of ZrO₂ were observed together with small peaks

assigned to tetragonal phase, which were detected from all the samples. Tetragonal phase grew stronger with increasing the calcination temperature while no obvious change was observed with the MgO content increasing from 10 to 30 mol% at a calcination temperature of 800 °C. Besides, the crystallinity of MgO was affected from both the calcination temperature and MgO content.

Figure 4 shows the CO₂-TPD profiles of 20-MgO/ZrO₂ calcined at different temperatures. Modification of m-ZrO₂ not only increased the weak basic sites α (desorbed at around 125 °C), which is similar with the support m-ZrO₂, but also enhanced the formation of a new kind of stronger basic sites β (desorbed at 200-500 °C). The results resemble those of CaO/m-ZrO₂ catalysts as reported in our previous work [23, 24, 26]. Both the number of basic sites α and β decreased with increasing calcination temperature. However, the specific surface areas of 20-MgO/ZrO₂ were also decreased as a similar rate to the basic sites decreased. Thus, the density of basic sites changed slightly when the calcination temperature increased from 600 to 800 °C, as summarized in Table 3.

3.3 Adsorptive interaction between a reactant and catalyst surface

To evaluate the adsorptive interaction between the reactant and catalysts such as 20-MgO/ZrO₂-800, pulse adsorption experiment was also carried out at a flow rate of 15 cm³ min⁻¹ at 220 °C. Figure 5 shows the TCD signals of three adsorption-desorption cycles for the injected adsorbates acetone, 1-decanol, 4P1OL and 1,5-PDO, of which the boiling points are 56.5, 231, 141 and 239 °C [27], respectively. Acetone and 1-decanol were used as references of low and high boiling points, respectively. The retention time of acetone, 1-decanol, 4P1OL and 1,5-PDO are 0.060, 0.072, 0.064, and 0.109 min, respectively. The FWHM of acetone, 1-decanol, 4P1OL and 1,5-PDO are 0.15, 0.14, 0.15, and 0.22 min,

respectively. The results obviously displayed the longer retention time and the broader peaks of 1,5-PDO than the others, despite the differences in molecular weight and boiling points, acetone, 1-decanol and 4P1OL, which showed almost the same retention time. Table 4 summarizes the FWHM and the retention time of 1,5-PDO and 4P1OL in the TCD signals over the catalysts such as m-ZrO₂-800, 20-MgO/ZrO₂-800, and 20-CaO/ZrO₂-800. Over 20-MgO/ZrO₂-800, the longest retention time and the broadest desorption peaks of 1,5-PDO were observed. This indicates that the adsorptive interaction between 1,5-PDO and 20-MgO/ZrO₂-800 is stronger than those between 1,5-PDO and the other catalysts.

Previously, we have reported that CaO/ZrO₂ selectively catalyzes the dehydration of 1,4-butanediol to produce 3-buten-1-ol [26]. CaO/ZrO₂ selectively produced 3-buten-1-ol from 1,4-butanediol whereas MgO/ZrO₂ showed inferior selectivity for the 3-buten-1-ol formation. We also conducted the pulse adsorption experiment for 1,4-butanediol and 3buten-1-ol. Table 4 also summarizes the FWHM and the retention time of 1,4-butanediol and 3-buten-1-ol in the TCD signals. Over 20-CaO/ZrO₂-800, the longest retention time and the broadest desorption peaks of 1,4-butanediol were observed. The large FWHM indicates the adsorptive interaction between 1,4-butanediol and CaO/ZrO₂ is stronger than the others, as well as the present results of 1,5-PDO and MgO/ZrO₂. As a reference, Table S3 summarizes adsorption data for various adsorbates on m-ZrO₂-800, 20-MgO/ZrO₂-800, and 20-CaO/ZrO₂-800.

4. Discussion

4.1 Structure of modified ZrO₂ catalysts related to 4P10L formation from 1,5-PDO

Well-crystallized pure m-ZrO₂ has been found selectively to produce unsaturated alcohols rather than t-ZrO₂ in the dehydration of 1,3-butanediol [28, 29], 2,3-butanediol [23,

24, 30], 1,4-butanediol [31-33] and 1,5-PDO [11]. High calcination temperatures, which can contribute to a high crystallinity of pure m-ZrO₂, obviously enhanced the formation rate of 4P1OL from 1,5-PDO (Table S1). This suggests that, on the surface of the pure m-ZrO₂, the density of active sites would increase with increasing calcination temperature. On the other hand, the calcination at high temperatures results in the rapid decrease in the specific surface area. Usually, the small specific surface area is not efficient for a high productivity. In this study, MgO was found to be efficient as a modifier in the selective formation to 4P1OL from 1,5-PDO. Especially, 20-MgO/ZrO₂ showed the highest 4P1OL selectivity (Table 2). However, in the m-ZrO₂ catalysts modified with MgO, calcination at temperatures higher than 900 °C could not enhance the formation rate of 4P1OL anymore (Table 3). The density of active sites on the surface of 20-MgO/ZrO₂ is not increased by calcination at high temperatures. Here, there are also no great changes with the density of basic sites over 20-MgO/ZrO₂ calcined at 600-900 °C. This suggests that the active sites are correlated with the basic sites.

Figure 3 indicates that modification of m-ZrO₂ with MgO at high calcination temperatures results in the formation of t-ZrO₂ and MgO phases. Especially, the peaks attributing to both t-ZrO₂ and MgO phases increased obviously with increasing calcination temperature from 600 to 900 °C. Since no 4P1OL was obtained from 1,5-PDO over pure MgO (1,5-PDO conversion at 400 °C, 11.9%; the main products: THP, 14.3%; HPA, 19.5%; DVL, 18.6%; unknown, 47.5%), the formation of MgO phase must waste the loaded MgO modifier and decreased the 4P1OL production. Furthermore, calcination at high temperatures made m-ZrO₂ transfer to t-ZrO₂ phase. Judging from the results of ineffective t-ZrO₂ catalyst for the 1,5-PDO dehydration as displayed in Table 1, the formed t-ZrO₂ phase would be inactive. Sometimes, calcination leads better crystallinity of m-ZrO₂ rather than the formation of t-ZrO₂ [34, 35]. In the present study, another possibility is that the

addition of MgO stabilized t-ZrO₂ transformed from m-ZrO₂. Several studies have showed the details on the preparation of t-ZrO₂ with MgO addition [36, 37]. Thus, the transformation from m-ZrO₂ to t-ZrO₂ also wasted a part of MgO. On the other hand, the dispersion of the inactive MgO and t-ZrO₂ occupied the limited specific surface area and resulted in decreasing the density of active sites. Thus, it could be explained that the formation rate of 4P1OL over MgO/ZrO₂ did not increase with increasing calcination temperature over 800 °C (Table 3), whereas that over pure m-ZrO₂ increased up to the temperature of 1000 °C, as shown in Table S1.

4.2 Proposed reaction mechanism in the dehydration of 1,5-PDO to 4P10L

Despite the negative changes of the structural transform of the ZrO₂ modified with MgO, the 4P1OL selectivity increased obviously and showed some correlation to the density of basic sites (Table 3). Besides, as described in the previous report [11], the more acidic catalysts such as SiO₂-Al₂O₃ showed almost full 1,5-PDO conversion and high selective productivity for THP rather than 4P1OL. The THP selectivity can be decreased efficiently by loading basic metal oxides such as Li₂O, Na₂O, K₂O, MgO, CaO, SrO, and BaO. It is reasonable that the dehydration of 1,5-PDO into 4P1OL also need some basic sites while the formation of THP from 1,5-PDO mostly depends on acidic sites. A small number of acidic sites was detected from the pure m-ZrO₂ while the modification with Li₂O made it difficult to be detected with the NH₃-TPD method [11]. In the present study, it is still a hard work to detect the acidity of MgO/ZrO₂ with the same method. It indicates the decreasing in the excess acidity, which is favorable for THP formation but not suitable for 4P1OL selectivity. Judging from the formation rate of 4P1OL, it is almost the same level between m-ZrO₂-800 and 20-MgO/ZrO₂, and the addition of basic MgO to ZrO₂ reduces the formation of THP (Table 2).

We have considered the selectivity to unsaturated alcohols strongly depends on the adsorption of diols on the specific surface [15, 38]. The adsorption model between 1,4-butanediol and Er_2O_3 was also successfully simulated with density functional theory (DFT) and paired interacting orbitals (PIO) calculation as acid-base concerted tridentate coordination mechanism: tridentate interactions between a position-2 H atom of diol and an O^{2-} on Er_2O_3 and between the two terminal OH groups and two Er^{3+} [38].

The mechanism of 4P1OL production over m- ZrO_2 should also be imaged as via the acid-base concerted tridentate coordination, in which the basic site is for adsorption of the position-2 H atom and the two acidic sites are for the two terminal OH groups (Scheme 1a), which is just as we imaged the adsorption structure for 1,4-butanediol [15, 26, 38, 39] and the work of Zhang's group [40]. On the other hand, THP was also produced via the cyclodehydration of 1,5-PDO, which quite resembles the THF formation from 1,4butanediol in its reaction [26]. Thus, we also speculate the acid-base concerted adsorption structure on ZrO_2 for the THP formation in Scheme 1b.

As to the 20-MgO/ZrO₂-800 catalyst, in which MgO content is 20 mol%, only small peaks belong to t-ZrO₂ and MgO phases were detected with the main diffraction peaks attributed to the support m-ZrO₂ (Fig. 3). However, basic sites generated on the surface of pure MgO cannot produce 4P1OL and t-ZrO₂ also showed low 4P1OL selectivity (Table 1). It indicates that most of Mg²⁺ exist in the major m-ZrO₂ for some new combination with Zr⁴⁺ such as Mg-O-Zr heterolinkages in the same way as CaO/ZrO₂ described in elsewhere [23-26, 40]. However, different from Ca-O-Zr, which can be easily aggregated into CaZrO₃ with the excess CaO or at high calcination temperatures, the new compound MgZrO₃ cannot be formed due to its thermal instability. In a similar way to the highly-dispersed Ca-O-Zr, new acid-base sites could be generated on the surface of MgO/ZrO₂ catalysts with a proper MgO content and then calcined at suitable temperatures. The promotion of 4P1OL

formation could be related to the new acid-base balance generated from the Mg-O-Zr linkages.

4.3 Adsorptive interaction between adsorbate and catalyst

The broadest FWHM for retention time of 1,5-PDO suggests the strongest adsorption between 1,5-PDO and MgO/ZrO₂ (Fig. 5 and Table 4). Table 4 compares the adsorptive interaction between adsorbates, such as 1,5-PDO, 4P1OL, 1,4-butanediol, and 3-buten-1-ol, and catalysts, such as m-ZrO₂, MgO/ZrO₂ and CaO/ZrO₂, together with the catalytic results of the selectivity to 4P1OL in the present dehydration of 1,5-PDO and that to 3-buten-1-ol in the previous dehydration of 1,4-butanediol [26]. The strongest adsorptive interaction between 1,5-PDO and MgO/ZrO₂ as well as between 1,4-butanediol and CaO/ZrO₂ is presented. The strongest interaction shows the combination of reactants and the better catalyst with high selectivity. Besides, there is no significant difference in the FWHM of the unsaturated alcohols over all the tested catalysts. This also suggests that the adsorptive interaction between 20-MgO/ZrO₂-800 and the target product, 4P1OL, is as weak as acetone and 1-decanol. The weak adsorption between the unsaturated alcohols and the catalysts would attribute to the desorption of unsaturated alcohols without further reaction. The strong adsorptive interaction between catalyst and reactant would be favorable for the formation of these unsaturated alcohols from the corresponding diols.

It is reasonable that the strong adsorptive interaction between 1,5-PDO and MgO/ZrO₂ contributed to the high 4P1OL selectivity. The difference between 4P1OL and 1,5-PDO is that 1,5-PDO has two terminal OH groups in its molecule. The two OH groups should be attributed to the adsorption of 1,5-PDO on the surface of catalysts. In addition, the dehydration of 1,5-PDO into 4P1OL also requires the elimination of one terminal OH group

and a position-2 H atom for the desorption of one water molecule. Thus, there must be some adsorption sites for the terminal OH groups and the position-2 H. On the surface of pure m-ZrO₂, two Zr⁴⁺ act as the Lewis acidic sites for the adsorption of the two OH groups while an O^{2-} act as the Lewis basic sites for that of a position-2 H, as imaged in Scheme 1a. Similarly, the formation of 4P10L from 1,5-PDO over MgO/ZrO₂ could be imaged as Scheme 1c, in which one of the Lewis acid (Zr⁴⁺) is replaced by Mg²⁺. It has been reported that the standard molar Gibbs free energy for Mg(OH)₂ formation from MgO is lower than that of Zr(OH)₄ formation from ZrO₂ [41]. On the surface of MgO/ZrO₂, Mg²⁺ strongly adsorbs one of the OH group and activates the elimination of the terminal -OH group from 1,5-PDO, as imaged in Scheme 1c. Due to the increase in the strength and density of basic sites, which must be generated from the O^{2-} of Mg-O-Zr, the elimination of the position-2 H atom should be promoted. After the elimination of one terminal OH group and the position-2 H, the formed 4P10L is adsorbed on the catalysts weakly. Finally, the desorption of 4P10L proceeds without further reaction. Thus, Scheme 1c is the most probable reaction mechanism for the high 4P10L selectivity over MgO/ZrO₂ catalysts.

5. Conclusions

Vapor-phase dehydration of 1,5-PDO was investigated over several modified monoclinic ZrO₂ catalysts. The formation of 4P1OL from 1,5-PDO was efficiently enhanced by the modification of m-ZrO₂ with MgO. A high 4P1OL selectivity of 83.3% at the 1,5-PDO conversion of 59.1% was obtained over 20-MgO/ZrO₂-800 at W/F=0.3 h and 400 °C. CO₂-TPD revealed that MgO supported on m-ZrO₂ and calcination at a proper temperature of 800 °C generated more basic sites for the formation of 4P1OL from 1,5-PDO. At temperatures higher than 800 °C, however, XRD patterns showed that excess MgO content and calcination MgO/m-ZrO₂ made the loaded Mg²⁺ move into ZrO₂ and promoted the transformation to tetragonal ZrO₂, which is not efficient for the 4P1OL formation from 1,5-PDO. In addition,

stable catalytic conversion of 96% with the 4P1OL yield of 72% was observed at W/F=1.8 h and 400 $^{\circ}$ C for 10 h of time on stream.

A pulse adsorption reveals that adsorptive interaction between 1,5-PDO and MgO/ZrO₂ is stronger than the other catalysts. The adsorption-desorption evaluation also displayed the stronger adsorptive interaction between 1,4-butanediol and CaO/ZrO₂, which shows the selective formation of 3-buten-1-ol in the dehydration of 1,4-butanediol [26]. These results help us to understand the acid-base concerted tridentate coordination adsorption for the formation unsaturated alcohols from alkanediols.

Appendix A. Supplementary data

Supplementary data to this article can be found online at a WEB page.

References

- [1] W. Wang, L. Hou, J. Sheng, M. Ren, Y. Tang, Exp. Polym. Lett. 10 (2016) 1026-1033.
- [2] W. Wang, L. Hou, S. Luo, G. Zheng, H. Wang, Macromol. Chem. Phys. 214 (2013) 2245-2249.
- [3] N. Narain, M. S. Galvão, M. S. Madruga, Food Chem. 102 (2007) 726-731.
- [4] Y. J. Cha, H. Kim, K. R. Cadwallader, J. Agric. Food Chem. 46 (1998) 1944-1953.
- [5] P. R. Krishna, K. Anitha, Tetrahedron Lett. 52 (2011) 4546-4549.
- [6] S. Rajaram, U. Ramulu, S. Aravind, K.S. Babu, Helv. Chim. Acta 98 (2015) 650-656.
- [7] M. D. Rvovic, V. M. Diva, R. Puchta, Z. M. Bugarči, J. Mol. Model. 17 (2011) 1251-1257.
- [8] L. A. Brooks, H. R. Snyder, Org. Syn. 25 (1945) 84-86.
- [9] R. Robinson, L. H. Smith, J. Chem. Soc. (1936) 195-196.
- [10] M. S. Kharasch, C. F. Fuchs, J. Org. Chem. 9, (1944) 359-372.
- [11] S. Sato, R. Takahashi, N. Yamamoto, E. Kaneko, H. Inoue, Appl. Catal. A 334 (2008) 84-91.
- [12] M. Segawa, S. Sato, M. Kobune, T. Sodesawa, T. Kojima, S. Nishiyama, N. Ishizawa, J. Mol. Catal. A 310 (2009) 166-173.
- [13] F. Sato, H. Okazaki, S. Sato, Appl. Catal. A 419-420 (2012) 41-48.
- [14] F. Sato, S. Sato, Catal. Commun. 27 (2012) 129-133.
- [15] S. Sato, F. Sato, H. Gotoh, Y. Yamada, ACS Catal. 3 (2013) 721-734.
- [16] R. Jayakumar, Y.S. Lee, S. Nanjundan, J. Appl. Polym. Sci. 92 (2004) 710-721.
- [17] L. Guang, R.J. Gaymans, Polym. 38 (1997) 4891-4896.
- [18] D. K. Lee, H. B. Tsai, W. J. Yu, R. S. Tsai, J. Macromol. Sci. Part A Pure Appl. Chem. 42 (2005) 85-93.
- [19] W. Xu, H. Wang, X. Liu, J. Ren, Y. Wang, G. Lu, Chem. Commun. 47 (2011) 3924-3926.
- [20] S. Koso, I. Furikado, A. Shimao, T. Miyazawa, K. Kunimori, K. Tomishige, Chem. Commun., 45 (2009) 2035-2037.
- [21] M. Chia, Y.J.P. Torres, D. Hibbitts, Q. Tan, H.N. Pham, A.K. Datye, M. Neurock, R.J. Davis, J.A. Dumesic, J. Am. Chem. Soc. 133 (2011) 12675-12689.
- [22] H.W. Wijaya, T. Kojima, T. Hara, N. Ichikuni, S. Shimazu, ChemCatChem, in press; doi:

10.1002/cctc.201700066.

- [23] H. Duan, Y. Yamada, S. Sato, Appl. Catal. A 487 (2014) 226-233.
- [24] H. Duan, Y. Yamada, S. Kubo, S. Sato, Appl. Catal. A 530 (2017) 66-74.
- [25] Q. Zhang, Y. Zhang, H. Li, C. Gao, Y. Zhao, Appl. Catal. A: Gen. 466 (2013) 233-239.
- [26] H. Duan, T. Hirota, S. Ohtsuka, Y. Yamada, S. Sato, Appl. Catal. A 535 (2017) 9-16.
- [27] CRC Handbook of Chemistry and Physics 82nd Ed., Ed. By D.R. Lide, CRC Press (2001).
- [28] N. Ichikawa, S. Sato, R. Takahashi, T. Sodesawa, J. Mol. Catal. A: Chem. 256 (2006) 106-112.
- [29] T. Nozawa, S. Sato, R. Takahashi, Top Catal. 52 (2009) 609-617.
- [30] H. Duan, D. Sun, Y. Yamada, S. Sato, Catal. Commun. 48 (2014) 1-4.
- [31] N. Yamamoto, S. Sato, R. Takahashi, K. Inui, Catal. Commun. 6 (2005) 480-484.
- [32] N. Yamamoto, S. Sato, R. Takahashi, K. Inui, J. Mol. Catal. A: Chem. 243 (2006) 52-59.
- [33] H. Inoue, S. Sato, R. Takahashi, Y. Izawa, H. Ohno, K. Takahashi, Appl. Catal. A 352 (2009) 66-73.
- [34] Z. Peng, X. Liu, S. Li, Z. Li, B. Li, Z. Liu, S. Liu, Sci. Rep. 7 (2017) 39847; doi: 10.1038/srep39847.
- [35] Y. Ikuma, T. Sugiyama, J. Okano, J. Mater. Res. 8 (993) 2757-2760.
- [36] O. Sahin, İ. Demirkol, H. Göcmez, M. Tuncer, H. Ali Cetinkara, H. Salih Güder, E. Sahin, A. R. Tuncdemirc, Acta Phy. Pol. A 123 (2013) 296-298.
- [37] J. Akhtar, S. K. Durrani, N. A. Chughtai, K. A. Shahid, J. Chem. Soc. Pak. 19 (1997) 93-103.
- [38] F. Sato, S. Sato, Y. Yamada, M. Nakamura, A. Shiga, Catal. Today 226 (2014) 124-133.
- [39] S. Sato, R. Takahashi, M. Kobune, H. Inoue, Y. Izawa, H. Ohno, K. Takahashi, Appl. Catal. A 356 (2009) 64-71.
- [40] Q. Zhang, Y. Zhang, H. Li, Y. Zhao, M. Ma, Y. Yu, Chinese J. Catal. 34 (2013) 1159-1166.
- [41] J. J. Bravo-Suárez, E. A. Páez-Mozo, S. T. Oyama, Quim. Nova 27 (2004) 601-614.

Catalyst	Conversion	Selectivity (mol %) ^b				
	(mol%)	4P1OL	THP	DVL	Others	
t-ZrO ₂ ^c	62.9	27.6	66.3	2.4	3.7	
m-ZrO ₂ -800	85.1	62.4	25.3	2.1	10.2	
1-Li ₂ O/ZrO ₂ -700	42.5	64.4	10.3	8.8	16.5	
1-Na ₂ O/ZrO ₂ -700	67.2	61.0	9.9	7.6	21.5	
1-K ₂ O/ZrO ₂ -700	54.6	57.4	7.8	8.5	26.4	
5-MgO/ZrO ₂ -800	58.1	77.7	6.6	4.3	11.4	
5-CaO/ZrO ₂ -800	79.4	67.3	14.0	4.0	14.8	
5-SrO/ZrO ₂ -800	61.6	46.8	17.5	8.8	26.8	
5-BaO/ZrO ₂ -800	50.5	49.4	16.2	9.2	25.2	

Table 1 Dehydration of 1,5-PDO over zirconia-based catalysts ^a

^a Average conversion and selectivity between 1 h to 5 h. Catalyst weight, W = 0.5 g; W/F =0.3 h.

Reaction temperature, 400°C; N₂ flow rate, 30 cm³ min⁻¹.

^b 4P1OL, 4-penten-1-ol; THP, tetrahydropyran; DVL, δ-valerolactone. Others include 1,4-pentadiene, pentanal, 1-

pentanol and 5-hydroxypentanal.

^c Cited from Ref. [11].

MgO content	S.A.	Conversion	Selectivity (mol %) ^b			Formation rate of 4P1OL	
(mol%)	$(m^2 g^{-1})$	(mol%)	4P1OL	THP	DVL	Others	$(mmol h^{-1} m^{-2})$
0	27.7	85.1	62.4	25.3	2.1	10.2	0.61
5	25.4	58.1	77.7	6.6	4.3	11.4	0.57
10	24.1	57.3	78.2	6.0	4.2	11.6	0.59
20	23.4	59.1	83.3	5.1	3.7	7.9	0.67
30	17.3	46.5	77.0	7.2	4.8	11.1	0.66

Table 2 Dehydration of 1,5-PDO over m-ZrO₂ modified with MgO^a

^a Average conversion and selectivity between 1 h to 5 h. Catalyst weight, W = 0.5 g; W/F =0.3 h.

Calcined at 800°C; Reaction temperature, 400°C; N2 flow rate, 30 cm3 min-1.

^b 4P1OL, 4-penten-1-ol; THP, tetrahydropyran; DVL, δ-valerolactone. Others include 1,4-pentadiene, pentanal, 1-pentanol

and 5-hydroxypentanal.

Calcination temperature	S.A.	Density of basic sites ^b	Conversio n	Selectivity (mol %) ^c			Formation rate of 4P1OL	
(°C)	$(m^2 g^{-1})$	(nm ⁻²)	(mol%)	4P1OL	THP	DVL	Others	$(mmol h^{-1} m^{-2})$
m-ZrO ₂ - 800	27.7	0.9	85.1	62.4	25.3	2.1	10.2	0.61
600	47.4	2.8	58.4	79.9	6.2	4.9	9.0	0.31
700	30.2	3.5	62.5	82.9	4.6	4.0	8.5	0.55
800	23.4	2.7	59.1	83.3	5.1	3.7	7.9	0.67
900	17.5	2.3	46.0	80.5	5.0	4.0	10.5	0.67
1000	8.5	-	43.4 ^d	80.3	5.2	4.3	10.2	0.65

Table 3 Dehydration of 1,5-pentanediol over 20-MgO/ZrO2 calcined at different temperatures ^a

^a Average conversion and selectivity between 1 h to 5 h. Catalyst weight, W = 0.5 g; W/F = 0.3 h.

Reaction temperature, 400°C; N2 flow rate, 30 cm3 min-1.

^b Based on the number of basic sites, which was detected with the CO₂-TPD method, and the specific surface area, which was measured with the BET method.

^c 4P1OL, 4-penten-1-ol; THP, tetrahydropyran; DVL, δ-valerolactone. Others include 1,4-pentadiene, pentanal, 1-pentanol and 5-hydroxypentanal.

^d Catalyst weight, W = 1.0 g; W/F = 0.6 h.

Catalyst ^a]	FWHM /min (r	Selectivity (mol %)			
	1,5-PDO	4P1OL	1,4-Butanediol	3-Buten-1-ol	4P1OL ^c	3-Buten-1- ol ^d
m-ZrO ₂	0.091 (0.18)	0.060 (0.14)	0.082 (0.18)	0.061 (0.14)	62.4	38.9
MgO/ZrO ₂	0.109 (0.22)	0.064 (0.15)	0.079 (0.15)	0.060 (0.15)	83.3	50.5 ^d
CaO/ZrO ₂	0.090 (0.19)	0.064 (0.14)	0.103 (0.19)	0.061 (0.14)	67.3 ^e	86.9 ^f

Table 4 Adsorption parameter of several reactants over zirconia-based catalysts

^a Catalyst: m-ZrO₂, m-ZrO₂-800; MgO/ZrO₂, 20-MgO/ZrO₂-800; CaO/ZrO₂, 20-CaO/ZrO₂-800.

^b Adsorption temperature, 220°C; He flow rate, 15 cm³ min⁻¹.

^c This work, the dehydration of 1,5-PDO at 400°C in Table 1.

^d The dehydration of 1,4-butanediol at 350°C; the data cited from Ref. [26].

^f CaO/ZrO₂ is 2-ZrO₂+7-CaO/ZrO₂-800 [26]

^e CaO/ZrO₂ is 5-CaO/ZrO₂-800.



Figure 1 Changes in catalytic activity of 20-MgO/ZrO₂-800 with reaction temperature. W/F = 0.3 h.



Figure 2 Long term test of dehydration of 1,5-PDO over 20-MgO/ZrO₂-800 at 400°C and W/F = 1.8

h.



Figure 3 XRD profiles of MgO/ZrO₂ modified with different MgO contents and calcined at different temperatures.



Figure 4 CO₂-TPD profiles of 20-MgO/ZrO₂ calcined at different temperature.



Figure 5 Changes in TCD signal of several adsorbates over MgO/ZrO₂ sample with time.

The dotted lines mean the injection points of each pulse.



Figure 6 Image of adsorption of 1,5-pentanediol and 4-penten-1-ol on MgO/ZrO₂.

(a)



Scheme 1 Proposed reaction mechanism for formation of 4P1OL (a) and THP (b) over m-ZrO₂ and 4P1OL over MgO/ZrO₂ (c).